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Abstract

ELECTROCHEMICAL REDUCTION OF DILUTE NITRIC ACID

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Dilute nitric acid is a major constituent of many radioactive liquid waste systems. The methods currently used for its disposal, such as neutralisation or reduction with formaldehyde, suffer from several disadvantages.

Electrochemical reduction of nitric acid generally gives rise to undesirable products, such as ammonia, which interfere in subsequent processing of the waste. An attempt to find an electrochemical reduction process which would reduce nitric acid to gaseous products, and would not require the addition of foreign ions to the system, led to an investigation of the behaviour of a graphite cathode in dilute (0.5 - 3N) nitric acid.

Current-voltage curves, determined by a potentiostatic method, were measured at different acid concentrations, at different temperatures, and in the presence of urea and sodium nitrite. Electrochemical reduction of nitric acid takes place at positive potentials, the products of reduction being mainly gaseous oxides of nitrogen. The presence of carbon dioxide has also been established among the products. The rate of the electrochemical reaction increases rapidly with increase in nitric acid concentration. There is evidence to show that the rate varies linearly with the concentration of nonionised nitric acid. At low acid concentrations, presence of nitrite increases the rate, while at high acid concentrations the addition of nitrite reduces the rate of the electrochemical reaction.

The rate is also reduced in the presence of urea. The results indicate that one of the electrochemical reactions involved is the reduction of nitrous acid, which

may be formed by the chemical reduction of the nitric acid by the graphite.

One of the possible reaction schemes is the following:

1. Chemical reduction

$$HNO_3 + C \rightarrow CO + HNO_2$$

$$2HNO_3 + C \rightarrow CO_2 + 2HNO_2$$

2. Electrochemical reduction

$$HNO_2 + e + H^+ \rightarrow NO + H_2O$$

3. Oxidation

$$CO + O \rightarrow CO_2$$

$$NO + O \rightarrow NO_2$$